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Reexamination of Synthetic Parkerite and Shandite

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Abstract

A reinvestigation of synthetic parkerite, $Ni_3Bi_2S_2$, has demonstrated that the unit cell is 4 times the volume of that previously reported (Michener and Peacock, 1943). It has monoclinic symmetry, most probable space group $C2/m$ with $a = 11.066$, $b = 8.085$, $c = 7.965$ Å, $\beta = 134.0°$. The larger cell was confirmed by single crystal X-ray diffraction data, but can be deduced from the presence of extra lines in the powder pattern of a specimen which has been annealed after grinding. This same technique revealed the rhombohedral distortion of shandite, $Ni_3Pb_2S_2$, space group $R\bar{3}m$, previously thought to be dimensionally cubic. The unit cell of shandite was found to be $a = 5.591$, $c = 13.579$ Å. The Sn analogue of shandite, $Ni_3Sn_2S_2$, reported for the first time, is hexagonal with $a = 5.465$, $c = 13.196$ Å. We were unable to synthesize any Mn, Fe, Co, or Cu analogs of the parkerite-shandite series.

Introduction

The impetus of solid state technology has created an increased interest in phases which crystallize in noncentrosymmetric space groups. Such phases often have interesting optical and/or electrical properties. Several reference books, including *Crystal Data* by Donnay *et al* (1963) and *Crystallographic Data on Metal and Alloy Structures* by Taylor and Kagle (1963), have listed the compound $Ni_3Bi_2S_2$ as belonging to the orthorhombic noncentrosymmetric space group C_{2v}^1-$Pmm2$ No. 25 of the *International Tables for X-ray Crystallography* (1952). These listings are the results of the paper by Michener and Peacock (1943) who state, in part ". . . . a study of the atomic arrangement, now in progress, indicates a structure with the symmetry of the space-group $Pmm2$-C_{2v}^1 (pyramidal class-$mm2$)". A later paper by Peacock and McAndrew (1950) on parkerite ($Ni_3Bi_2S_2$) and shandite ($Ni_3Pb_2S_2$) did not contribute any further information on the structure of parkerite.

A study of parkerite, shandite, and other materials of similar chemical nature was therefore initiated in order to further determine the crystallographic nature of these phases and their chemical and physical properties.

Experimental

The compositions examined in this study are indicated in Table 1. The specimens were prepared by heating about 10 grams of the appropriate mixture of the end member elements in evacuated, sealed, silica-glass tubes of 1.2 cm inner diameter and 8-10 cm in length. Heat treatment varied from 500°-600°C to 1000°-1100°C depending on the chemical nature of the mixture. In general an attempt was made to obtain complete melting of the mixture which was then heat treated in a "rocking furnace" in order to insure chemical homogeneity. For those materials which appeared to form a single phase, appropriate experiments were performed to obtain single crystals by the Bridgman technique.

For the composition 3Fe:2Bi:2S, the mixture was finally heated inductively to about 1500°C in a graphite crucible contained in an evacuated silica-glass tube in order to obtain complete melting.

Results

Table 1 shows that in addition to the previously reported parkerite and shandite only one new phase structurally related to this series has been found in the present study, namely $Ni_3Sn_2S_2$. Although the Sn analogue of shandite was synthesized, the Sb analogue of parkerite apparently does not exist, nor do any of the phases with Mn, Fe, Co, or Cu substituted for Ni. No attempt was made in this study to synthesize any Se or Te phases.

The X-ray powder diffraction lines of the single phases (synthetic parkerite, shandite, and $Ni_3Sn_2S_2$) were all rather broad, apparently due to strain induced by grinding. If the previously ground powder was reheated in evacuated silica glass capsules at

~600°C, this strain could be annealed out. Very sharp X-ray diffraction patterns then revealed additional details which were not observed by Michener and Peacock (1943) or Peacock and McAndrew (1950).

Parkerite, $Ni_3Bi_2S_2$

The mineral parkerite was named by Scholtz (1936) for material from South Africa and later was described and characterized by Michener and Peacock (1943) in a study of ore minerals of the Sudbury area. For the mode of occurrence the reader is directed to this work of Michener and Peacock (1943). Parkerite was found to be identical to the synthetic product $Ni_3Bi_2S_2$ previously prepared by Schenck and von der Forst (1939). From rotation and Weissenberg photographs of a cleavage fragment of the mineral, Michener and Peacock described the unit cell as orthorhombic $a = 4.02$ Å, $b = 5.52$ Å, $c = 5.72$ Å, space group *Pmm*2, $Z = 1$. They state that "fragments of natural and artificial parkerite are all twinned intergrowths consisting of tablets bounded by the eminent basal cleavage and transversed by twin lamellae which are parallel to planes of the form (111) of the main tablet."

The X-ray powder diffraction pattern for an annealed specimen of synthetic parkerite is compared in Table 2 with that of Michener and Peacock (1943). On the basis of single crystal precession data, the unit cell cited by Michener and Peacock can be transformed by interchanging *a* and *b* and doubling all three axes. Indexing of the powder pattern has been done on this orthogonal *F*-centered monoclinic cell with the former *a* as the unique axis, for convenience. The indexing on the body-centered and *C*-centered cells are shown for comparison.

The differences between the present cell and that of Michener and Peacock are readily discernible in the powder pattern of material which has been annealed *after* grinding. The annealed specimen was prepared for the powder pattern without mechanical deformation. With such treatment the X-ray pattern shows very sharp narrow peaks. Numerous superstructure lines can be seen that are not accounted for by the unit cell of Michener and Peacock (1943). Most notable is the extra peak at 5.672 Å. Single crystal data indicate that this is actually a first order reflection of the strong reflection at 2.836 Å. If the orientation is kept the same, all three axes would have to be doubled. It was proven that this is the true unit cell by taking numerous zero and first level precession patterns. The *h*1*l* pattern was the most significant, indicating monoclinic symmetry and showing numerous weak spots present only for *h* and $l = 2n + 1$ (*F*-centered cell).

The crystallographic data for parkerite, as found in the present study, are therefore *F*-centered monoclinic, $a = 11.066 \pm 0.001$, $b = 8.085 \pm 0.001$, $c = 11.458 \pm 0.001$, $\beta = 90.0°$, calculated specific gravity 8.53, measured 8.50. The new cell has eight times the volume of the previous subcell and a formula of $8(Ni_3Bi_2S_2)$. A *C*-centered cell may be chosen according to convention; this reduces the *c*-dimension to 7.965 ± 0.001 and changes β to 134.0°. However, the body-centered cell has the smallest *a* and *c* parameters, with $a = c = 7.965$ Å and $\beta = 92°$. The probable space groups of the *C*-centered cell are *C*2/*m*, No. 12), *Cm* (No. 8) or *C*2 (No. 5). The discovery of the larger true cell of parkerite obviates the necessity of listing it as *Pmm*2 (No. 25) and removes it from the list of probable non-centrosymmetric crystals.

The probable, idealized, atomic positions—taken from Fleet's (1973) structure of parkerite but modified for the monoclinic system—are shown in Table 3 for the space group *C*2/*m* (No. 12). The *b* and *c* axis of Fleet's orientation are interchanged to conform with the observed monoclinic symmetry. The powder pattern intensities calculated from these

TABLE 1. Results of Attempted Synthesis of Phases Structurally Similar to Parkerite and Shandite†

Composition	Visual Observation	X-ray Analyses
$Ni_3Bi_2S_2$	Homogeneous	Parkerite
$Ni_3Pb_2S_2$	Homogeneous	Shandite + PbS_{trace}
$Ni_3Sn_2S_2$	Homogeneous	Sn-Shandite + SnS_{trace}
$Ni_3Sb_2S_2$	Homogeneous	Single phase cubic solid solution of NiSbS-ullmanite
$Ni_3Cd_2S_2$	Incomplete reaction-free Cd	--
$Co_3Bi_2S_2$	Small spherical shaped particles*	Mostly Bi metal**
$Co_3Pb_2S_2$	Incomplete reaction	Mostly pentlandite type phase Co_9S_8-Co_4S_3
$Fe_3Bi_2S_2$	Incomplete reaction-free Fe	Contains free Bi
$Mn_3Bi_2S_2$	Incomplete reaction-free Mn	--
$Mn_3Pb_2S_2$	Incomplete reaction-free Mn	--
$Cu_3Bi_2S_2$	Incomplete reaction-free Cu	--

†*Ten gram batches of appropriate amounts of the elements were melted in sealed evacuated glass tubes.*
**Many of the particles are attracted by magnet.*
***Some particles have monoclinic distortion of Bi structure.*

TABLE 2. X-ray Diffraction Powder Pattern of Synthetic Parkerite $Ni_3Bi_2S_2$ (CuKα Radiation)

Michener and Peacock (1943)		Present Study							
d_{obs}	hkℓ reported	d_{obs}	F.C. hkℓ a/	B.C. hkℓ b/	C.C. hkℓ c/	$2\theta_{obs}$	$2\theta_{calc}$ d/	I_{obs}	I_{calc}
5.8	001	{5.727	002	$10\bar{1}$	001	15.46	15.45	20	23
		5.672}	111	110/011	$11\bar{1}/110$	15.61	15.61	5	11
4.01	{100	4.039	020	020	020	21.99	21.97	24	27
	011}	3.976	202	200/002	$20\bar{2}/200$	22.34	22.32	32	58
3.29	101	3.2996	{022	$12\bar{1}$	021	27.00	{26.97	3	5
			113}	$21\bar{1}/11\bar{2}$	$11\bar{2}/111$		27.03}		5
--	---	3.2177	311	211/112	$31\bar{2}/311$	27.70	27.68	1	1
2.85	{002	2.8643	004	$20\bar{2}$	002	31.20	31.20	64	24
	111}	2.8360	222	220/022	$22\bar{2}/220$	31.52	31.52	100	100
--	---	2.7676	400	202	$40\bar{2}$	32.32	32.33	11	18
2.56	012	{2.5531	131	130/031	$13\bar{1}/130$	35.12	35.13	3	1
		2.5447}	204	$30\bar{1}/10\bar{3}$	$20\bar{3}/201$	35.24	35.25	3	1
--	---	2.4900	402	301/103	$40\bar{3}/40\bar{1}$	36.04	36.02	2	3
2.33	102	2.3358	024	$22\bar{2}$	022	38.51	38.49	54	42
2.28	120	2.2823	420	222	$42\bar{2}$	39.45	39.44	22	35
2.15	112	2.1602	133	$23\bar{1}/13\bar{2}$	$13\bar{2}/131$	41.78	41.79	3	<1
--	---	2.1543	224	$32\bar{1}/123$	$22\bar{3}/221$	41.90	41.93	1	1
2.12	121	2.1205	422	321/123	$42\bar{3}/421$	42.60	42.59	4	5
2.02	200	2.0209	040	040	040	44.81	44.81	20	21
1.984	022	1.9894	404	400/004	$40\bar{4}/400$	45.56	45.55	24	34
1.897	201	{1.9095	006	303	003	47.58	47.58	2	<1
		1.9050	042	$14\bar{1}$	041	47.70	47.67	2	2
		1.8930}	315	$41\bar{1}/11\bar{4}$	$31\bar{4}/311$	48.02	48.04	1	<1
1.802	013	{1.8050	206	$40\bar{2}/20\bar{4}$	$20\bar{4}/202$	50.52	50.52	13	9
		1.8018}	242	240/042	$24\bar{2}/240$	50.62	50.61	13	13
1.782	122	1.7853	424	420/024	$42\bar{4}/420$	51.12	51.12	9	7
--	---	1.7526	602	402/204	$60\bar{4}/60\bar{2}$	52.06	52.05	2	7
1.723	103	1.7260	026	$32\bar{3}$	023	53.01	52.99	4	2
1.645	{113	{1.6513	044	$24\bar{2}$	042	55.61	55.61	11	9
	202}	1.6477	226	$42\bar{2}/22\bar{4}$	$22\bar{4}/222$	55.74	55.72	23	20
		1.6319}	440	242	$44\bar{2}$	56.33	56.33	7	6
1.611	131	1.6104	622	422/224	$62\bar{4}/62\bar{2}$	57.15	57.15	7	19
--	---	1.5828	244	$34\bar{1}/14\bar{3}$	$24\bar{3}/241$	58.24	58.26	1	<1
--	---	1.5784	335	$43\bar{1}/13\bar{4}$	$33\bar{4}/331$	58.42	58.44	2	<1
1.431	004	1.4322	008	$40\bar{4}$	004	65.07	65.07	17	5
1.415	222	1.4177	444	440/044	$44\bar{4}/440$	65.82	65.81	20	18
1.385	{014	{1.3879	{046	$34\bar{3}$	043	67.42	{67.41	1	<1
	203}		137}	$43\bar{3}/33\bar{4}$	$13\bar{4}/133$		67.42}		
		1.3863	208	$503/30\bar{5}$	$20\bar{5}/203$	67.51	67.50	2	<1
		1.3830	800	404	$80\bar{4}$	67.69	67.68	4	3
		1.3807}	353	350/053	$35\bar{3}/350$	67.82	67.82	2	<1
1.345	{104	1.3498	028	$42\bar{4}$	024	69.59	69.58	5	2
	213}	1.3465	246	$44\bar{2}/24\bar{4}$	$24\bar{4}/242$	69.79	69.80	6	5
1.324	033	1.3261	606	600/006	$60\bar{6}/600$	71.02	70.99	3	5
--	---	1.3088	820	424	$82\bar{4}$	72.11	72.11	1	1
--	---	1.2971	551	352/253	$55\bar{3}/552$	72.86	72.85	1	<1
1.270	{311	1.2765	262	260/062	$26\bar{2}/260$	74.23	74.25	3	6
	024}	1.2719	408	$60\bar{2}/20\bar{6}$	$40\bar{6}/402$	74.54	74.55	3	4
--	---	1.2605	626	620/026	$62\bar{6}/620$	75.34	75.34	3	7
--	---	1.2457	804	602/206	$80\bar{6}/80\bar{2}$	76.39	76.40	2	2
1.211	{302	1.2194	064	$26\bar{2}$	062	78.35	78.35	3	4
	124}	1.2133	428	$62\bar{2}/22\bar{6}$	$42\bar{6}/422$	78.82	78.82	7	7
1.186	312	1.1908	{264	$36\bar{1}/16\bar{3}$	$26\bar{3}/261$	80.61	{80.62	3	<1
			824}	622/226	$82\bar{6}/82\bar{2}$		80.64}		5
1.165	141*	1.1682	048	$44\bar{4}$	044	82.50	82.47	4	4
1.140	214	1.1431	248	444	$84\bar{4}$	84.73	84.71	3	3
1.119	015	1.1220	2,0,10	$60\bar{4}/40\bar{6}$	$20\bar{6}/204$	86.71	86.72	4	1
--	---	1.1192	842	543/345	$84\bar{5}/84\bar{3}$	86.98	86.95	3	<1
--	---	1.1159	464	460/064	$46\bar{4}/460$	87.30	87.32	3	1
--	---	1.1093	646	640/046	$64\bar{6}/640$	87.95	87.98	3	3
1.078	115	{1.0809	2,2,10	$62\bar{4}/42\bar{6}$	$22\bar{6}/224$	90.90	90.88	6	5
		1.0766}	448	$64\bar{2}/24\bar{6}$	$44\bar{6}/442$	91.36	91.38	3	4
--	---	1.0692	662	462/264	$66\bar{4}/66\bar{2}$	92.18	92.21	3	4
--	---	1.0605	844	642/246	$84\bar{6}/84\bar{2}$	93.16	93.17	2	2
--	---	1.0494	10,2,2	624/426	$10,2,\bar{6}/10,2,\bar{4}$	94.45	94.46	2	4
--	---	1.0241	4,2,10	$72\bar{3}/32\bar{7}$	$42\bar{7}/423$	97.55	97.56	2	<1
--	---	.9949	808	800/008	$80\bar{8}/800$	101.46	101.46	2	2
0.978	{304	.9812	{068	$46\bar{4}$	064	103.45	{103.42	3	2
	215}		2,4,10}	$64\bar{4}/44\bar{6}$	$24\bar{6}/244$		103.48}		
0.944	{420	.9462	6,2,10	$82\bar{2}/22\bar{8}$	$62\bar{8}/622$	109.00	108.99	3	4
	135	.9453	666	660/066	$66\bar{6}/660$	109.14	109.14	2	4
	333}								
0.927	106	.9292	0,2,12	$62\bar{6}$	026	111.99	111.98	4	3
0.923	324	.9251	468	$66\bar{2}/26\bar{6}$	$46\bar{6}/462$	112.75	112.78	2	3
0.913	116	.9146	864	662/266	$86\bar{6}/66\bar{2}$	114.75	114.73	2	2
0.901	026	.9027	4,0,12	$80\bar{4}/40\bar{8}$	$40\bar{8}/404$	117.15	117.18	2	2
--	---	.9010	484	480/084	$48\bar{4}/480$	117.50	117.49	3	5
--	---	.8931	086	$38\bar{3}$	083	119.20	119.17	2	<1

* *Misprint*

a/ *The unit cell of Michener and Peacock has been transformed on the basis of the single crystal data by interchanging a and b and doubling all three axes. The indexing has been done on a face centered orthorhombic cell although the observed symmetry is monoclinic. For instance, although the (111) peak is easily discernable the (11$\bar{1}$) apparently has zero intensity.*

b/ *The true monoclinic cell indexed on the basis of body centered symmetry with the shortest possible reciprocal vectors. a=7.965Å, b=8.085Å, c=7.965Å, β=92°.*

c/ *The conventional monoclinic cell indexed on the basis of C - centered symmetry. a=11.066Å, b=8.085Å, c=7.965Å, β=134°.*

d/ *Calculated on the basis of an orthorhombic unit cell with a=11.0662Å, b=8.0845Å, c=11.4576Å.*

atomic positions are in good qualitative agreement with the observed values (see Table 2), as well as with the unobserved values. However, there are still some differences in detail and the atomic parameters obviously need refinement.

It is apparent that the structure proposed by Fleet (1973) is only an average and his proposed disordered arrangement of his Ni(2) in half occupancy is incorrect. In reality this Ni atom (Ni(3) of Table 3) is apparently ordered, with adjacent subcells either occupied or empty. This explains the negative temperature factor observed by Fleet for his Ni(2) atom as well as the poor $R(0.096)$ for the "refined" cell. The ordering of this Ni atom gives rise to the superstructure requiring the larger cell. This can be seen in the calculated intensities (Table 2) where appreciable intensity occurs in many superstructure spots (those with k odd). The monoclinic structure has fewer symmetry-fixed parameters, as only 4 Ni atoms, Ni(2), are in special crystallographic positions. The proposed unrefined atomic positions are shown in Figure 1, together with the conventional orientation of the unit cell in the C-centered orientations and the orthorhombic subcell of Fleet (1973), and Michener and Peacock (1943).

TABLE 3. Probable Atomic Positions for Parkerite, $Ni_3Bi_2S_2$ (unrefined parameters)*

4 Bi(1)	in	(i)	x0z	(x∿1/4, z∿1/4)
4 Bi(2)	in	(i)	x0z	(x∿1/4, z∿3/4)
4 Ni(1)	in	(g)	0y0	(y∿1/4)
4 Ni(2)	in	(e)	1/4 1/4 0	
4 Ni(3)	in	(i)	x0z	(x∿0.0185, z∿0.196)
8 S	in	(j)	xyz	(x∿0, y∿1/4, z∿1/4)

* *Z = 4, Space group* C2/m, *No. 12;* *a=11.066, b=8.085, c=7.965Å, β=134°*

Shandite, $Ni_3Pb_2S_2$

The mineral shandite was originally described and named by Ramdohr (1950) from material from Trial Harbour, Tasmania. It was found to have the composition $Ni_3Pb_2S_2$ and was described as rhombohedral (pseudocubic) a = 11.15, c = 13.66 Å, α_{rh} = 90.0°, a_{rh} = 7.88 Å; or possibly a smaller unit cell with α_{rh} = 60°, a_{rh} = 5.576 Å. Peacock and McAndrew (1950) found a pseudocubic face centered rhombohedral lattice with a_{rh} = 5.576 Å, α_{rh} = 60°, $R\bar{3}m$, Z = 1; Pb(1) at 000; Pb(2) at 1/2, 1/2, 1/2; 3Ni at 1/2, 0, 0; 2S at xxx, x = 0.285.

The X-ray powder diffraction pattern for an annealed specimen of synthetic shandite is compared in Table 4 with that of Peacock and McAndrew (1950). The annealed specimen shows line splitting indicative of the true rhombohedral structure as opposed to the findings of Peacock and McAndrew who thought shandite to be dimensionally cubic although symmetrically rhombohedral. The pattern could easily be indexed on a hexagonal basis using the relative intensities calculated by Peacock and McAndrew (1950) as a guide to determine the nature of the line splitting. The crystallographic conclusions of Peacock and McAndrew for synthetic shandite are thus verified in the present work, not only by single crystal data, but also by the powder diffraction pattern itself. The unit cell dimensions of the hexagonal cell, refined by least squares analysis of the powder

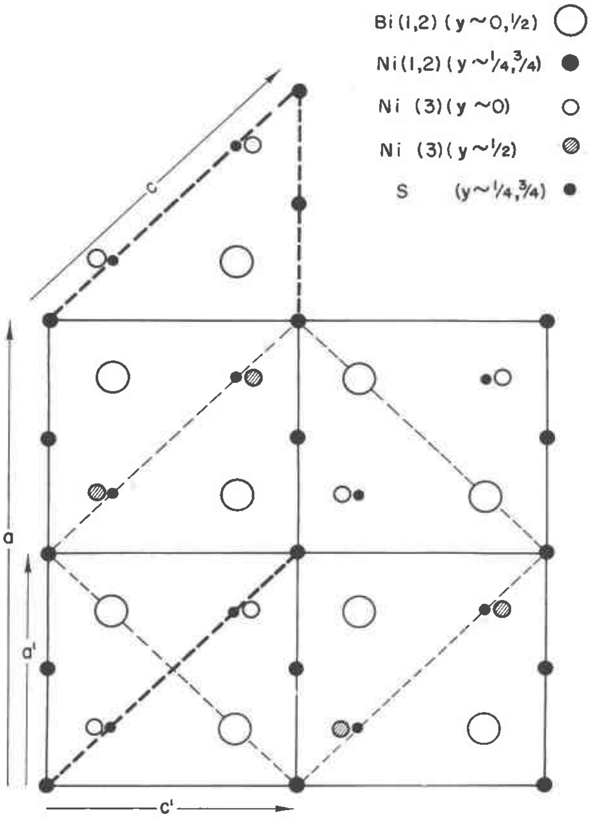

FIG. 1. Probable atomic positions projected onto (010) for parkerite, $Ni_3Bi_2S_2$. Four orthorhombic subcells (edges a' and c'), as reported by Michener and Peacock (1943) and by Fleet (1973), are compared to the larger F-centered orthogonal cell (edges $2a'$ and $2c'$), the true C-centered monoclinic unit cell (edges a and c), and the body centered cell (light dashed lines).

TABLE 4. X-ray Diffraction Powder Pattern of Synthetic Shandite, $Ni_3Pb_2S_2$ (Cu$K\alpha$ Radiation)

Peacock and McAndrew (1950)		Present Study					
d_{obs}	Cubic hkℓ	d_{obs}	hex hkℓ a/	$2\theta_{obs}$	$2\theta_{calc}$ a/	I_{obs}	I_{calc} b/
4.54	111	4.555	101	19.47	19.45	8	4
		4.525	003	19.60	19.60	12	13
3.96	002	3.943	012	22.53	22.54	84	100
2.79	022	2.7937	110	32.01	31.99	100	97
		2.7793	104	32.18	32.18	98	86
2.38	113	2.3822	021	37.73	37.71	18	13
		2.3774	113	37.81	37.79	18	6
		---	015	---	37.95	--	0
2.27	222	2.2806	202	39.48	39.49	81	80
		2.2619	006	39.82	39.80	29	31
1.969	004	1.9714	024	46.00	46.01	86	73
1.803	133	---	211	---	50.27	--	1
		1.8064	205	50.48	50.46	11	8
		1.8004	107	50.66	50.65	6	2
1.760	024	1.7660	122	51.72	51.69	25	23
		1.7587	116	51.95	51.94	31	30
1.609	224	1.6135	300	57.03	57.02	26	16
		1.6104	214	57.15	57.13	42	30
		1.6020	018	57.48	57.49	15	11
1.506	115 333	1.5199	303	60.90	60.89	1	1
		---	125	---	61.00	--	0
		1.5136	027	61.18	61.17	1	1
		1.5083	009	61.42	61.40	1	1
1.391	044	1.3978	220	66.88	66.89	16	25
		1.3899	208	67.31	67.32	16	20
---	135	---	131	---	70.40	--	<1
		1.3356	223	70.44	70.45	2	2
		1.3310	217	70.72	70.71	2	1
		---	119	---	70.92	--	0
1.309	006 244	1.3175	312	71.56	71.57	7	9
		1.3141	306	71.77	71.78	14	11
		1.3073	1,0,10	72.20	72.19	5	8
1.244	026	1.2489	134	76.16	76.17	10	13
		1.2448	128	76.46	76.48	11	10
---	335	1.2058	401	79.40	79.42	3	1
		---	315	---	79.57	--	0
		---	0,1,11	---	80.17	--	<1
1.187	226	1.1919	042	80.52	80.54	9	10
		1.1891	226	80.75	80.74	17	23
		1.1842	0,2,10	81.15	81.14	9	12
1.135	444	1.1403	404	84.99	85.00	9	12
		1.1315	0,0,12	85.80	85.80	4	3
---	117 155	---	321	---	88.18	--	<1
		1.1048	045 137	88.40	88.32 88.47	2	1 1
		---	309	---	88.67	--	<1
		---	2,0,11	---	88.92	--	1
1.089	046	1.0961	232	89.30	89.29	4	5
		1.0903	2,1,10	89.90	89.88	6	9
1.052	246	1.0565	410	93.61	93.61	10	9
		1.0557	324	93.71	93.71	11	10
		1.0531	318	94.01	94.01	11	6
		1.0489	1,1,12	94.50	94.51	5	3
1.024	137 355	---	413	---	96.95	--	1
		---	235	---	97.04	--	0
		---	407	---	97.20	--	<1
		1.0252	229	97.41	97.40	3	3
		---	1,2,11	---	97.64	--	<1
		---	1,0,13	---	97.94	--	<1
0.983	008	.9856	048	102.81	102.81	5	8
---	337	---	051	---	105.78	--	<1
		---	327	---	106.09	--	1
		---	0,2,13	---	106.86	--	1
0.954	028 446	.9586	502	106.94	106.93	2	2
		.9573	416	107.15	107.14	6	11
		.9548	1,3,10	107.56	107.55	6	8
		.9511	0,1,14	108.17	108.18	4	4
0.926	228 066	.9317	330	111.50	111.52	4	4
		.9312	054	111.62	111.62	6	3
		.9295	238	111.94	111.94	6	6
		.9264	3,0,12	112.50	112.48	4	5
---	157 555	.9128	241 333	115.10	115.08 115.13	3	2 <1
		---	505	---	115.24	--	0
		---	3,1,11	---	115.90	--	<1
		---	2,1,13	---	116.23	--	<1
0.903	266	.9068	422	116.30	116.30	5	7
		.9037	4,0,10	116.95	116.97	6	10
		.9004	2,0,14	117.62	117.63	5	11

a/ *Calculated on the basis of a hexagonal cell with -h+k+ℓ=3n and a=5.5907Å, c=13.579Å.*

b/ *Taken from Table 2 of Peacock and McAndrew (1950) recalculated on the basis of the strongest peak (012) as 100.*

TABLE 5. X-ray Diffraction Powder Pattern of Synthetic Sn-Shandite, $Ni_3Sn_2S_2$ (Cu$K\alpha$ Radiation)

d_{obs}	hkℓ a/	$2\theta_{obs}$	$2\theta_{calc}$ a/	I_{obs}
4.458	101	•19.90	19.91	10
4.401	003	20.16	20.17	18
3.844	012	23.12	23.11	52
2.7322	110	32.75	32.75	100
2.7065	104	33.07	33.07	65
2.3294	021	38.62	38.62	32
2.3219	113	38.75	38.76	25
---	015	--	39.04	--
2.2287	202	40.44	40.46	76
2.2000	006	40.99	41.00	38
1.9233	024	47.22	47.23	85
---	211	--	51.51	--
1.7619	205	51.85	51.85	17
1.7509	107	52.20	52.19	12
1.7266	122	52.99	52.99	15
1.7134	116	53.43	53.43	25
1.5779	300	58.44	58.45	16
1.5730	214	58.64	58.66	33
1.5578	018	59.27	59.28	20
1.4850	303	62.49	62.49	5
1.4810	125	62.68	62.69	5
---	027	--	62.99	--
1.4659	009	63.40	63.39	5
1.3662	220	68.64	68.63	33
1.3531	208	69.40	69.39	24
---	131	--	72.27	--
1.3048	223	72.36	72.36	8
1.2977	217	72.82	72.83	6
---	119	--	73.20	--
1.2874	312	73.50	73.50	4
1.2820	306	73.86	73.86	6
1.2711	1,0,10	74.60	74.60	8
1.2198	134	78.32	78.33	14
1.2125	128	78.88	78.87	17
---	401	--	81.63	--
---	315	--	81.89	--
1.1645	042	82.82	82.81	8
---	0,1,11	--	82.97	--
1.1605	226	83.17	83.17	26
1.1525	0,2,10	83.88	83.88	13
1.1137	404	87.52	87.51	11
1.0996	0,0,12	88.94	88.93	6
---	321	--	90.76	--
1.0797	045	91.03	91.03	6
1.0772	137	91.30	91.29	5
---	309	--	91.64	--
---	232	--	91.93	...
---	2,0,11	--	92.09	--
1.0619	2,1,10	93.00	93.00	8
1.0329	410	96.45	96.46	7
1.0313	324	96.65	96.63	7
1.0271	318	97.17	97.17	6
1.0217	1,1,12	98.06	98.06	5
---	413	--	100.01	--
---	235	--	100.19	--
---	407	--	100.46	--
.9996	229	100.82	100.82	8
---	1,2,11	--	101.26	--
---	1,0,13	--	101.81	--
.9615	048	106.48	106.48	7
---	051	--	109.34	--
---	327	--	109.90	--
---	502	--	110.58	--
.9349	416	110.96	110.96	7
.9329	0,2,13	111.32	111.32	9
.9307	1,3,10	111.72	111.72	8
.9244	0,1,14	112.87	112.87	6

a/ *Calculated on the basis of a hexagonal cell with -h+k+ℓ=3n and a=5.4652Å, c=13.1957Å.*

data, were found to be $a = 5.591 \pm 0.001$, $c = 13.579 \pm 0.001$ Å, calculated specific gravity 8.87, measured 8.65.

"Sn-Shandite", $Ni_3Sn_2S_2$

The new compound $Ni_3Sn_2S_2$ was synthesized in the present study by melting the constituent elements in a sealed, evacuated, silica-glass tube. The X-ray diffraction powder pattern of the annealed material is given in Table 5. It may be noted that the hexagonal line splitting of Sn-shandite is more exaggerated than that of the Pb-shandite. However, it seems likely that the two phases would form a complete series of solid solutions as they have the same rhombohedral symmetry, $R\bar{3}m$, and very similar unit cell dimensions. Indeed, Sn (as well as Cu) was identified in spectrographic analyses of $Ni_3Bi_2S_2$ by Michener and Peacock (1943). The refined unit cell dimensions of the hexagonal cell of $Ni_3Sn_2S_2$ were found to be $a = 5.465 \pm 0.001$, $c = 13.196 \pm 0.001$ Å. The calculated specific gravity is 6.97; however, the single crystal fragments available were not large enough for accurate measurement. The synthesized boule seemed to contain three phases with the specific gravity at the top measuring 6.41 and the bottom 7.37, possibly indicating incongruent melting.

Discussion

The reason for the occurrence of the sub-sulfide phases in the parkerite-shandite series remains a mystery. Ni is apparently the only transition metal to form this series although there is no data on the amount of Mn, Fe, Co, or Cu which might be incorporated in solid solution with the Ni compounds. The obvious argument that NiS is the only one of the series with a low-melting point, and thus makes synthesis easy, does not appear to be the explanation. Considerable effort was spent in obtaining complete melting for the 3Fe:2Bi:2S composition without any success in the formation of the phase. Craig, Barton, and Sepenuk (1971) in an investigation of the ternary Fe-Bi-S system also did not report any phase at this composition.

There seems to be no logical reason for Sn to substitute for Pb in shandite while Sb does not substitute (completely) for Bi in parkerite. Perhaps a study of ternary selenides and tellurides of these metals may help clarify the crystal chemical principles underlying the formation of these chalcogenides.

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